

The confined hydrogen atom with a moving nucleus

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Abstract. We study the hydrogen atom confined to a spherical box with impenetrable walls but, unlike earlier pedagogical articles on the subject, we assume that the nucleus also moves. We obtain the ground-state energy approximately by means of first-order perturbation theory and by a more accurate variational approach. We show that it is greater than the one for the case in which the nucleus is clamped at the center of the box. Present approach resembles the well-known treatment of the helium atom with clamped nucleus.

1. Introduction

Confined quantum-mechanical models have proved to be suitable first approximations for estimating the effect of pressure on the spectral lines of atoms and molecules or the effect of their neighbours in condense media. Several such models have been proposed for pedagogical purposes in introductory courses on quantum mechanics [1–20]. Among them we mention the quantum bouncer [2,3,6], the harmonic oscillator [8,12,13,16,18,20] and the hydrogen atom [7,9,11,12,14,15,17,19]. Such models have also been useful for the discussion of semiclassical approaches [6,7], the variational method [12,15,20] and perturbation theory [3,18,20]. Regarding the latter approach we mention that the sum over states is impractical for the calculation of corrections of order greater than the first one [3,18,20]. It is preferable either to integrate the perturbation equations directly [21] or to make use of the hypervirial and Hellmann–Feynman theorems [21,22].

In the case of the harmonic oscillator, most studies refer to the case of a particle that moves in a box under the effect of a potential of the form $V(x) = k(x - x_0)^2/2$ as if it were tied to the point x_0 by means of a spring of force constant k [8,12,16,18,20]. If we assume that the Hooke’s force is due to the interaction between two particles then we have a model similar to the one discussed by Tanner [13] who showed that it is not possible to separate the center of mass and internal degrees of freedom in the usual way because of the effect of the boundary conditions. Amore and Fernández [23] have recently discussed this problem in greater detail.

The usual model for the confined hydrogen atom suffers from the same limitation: the nucleus is considered to be clamped somewhere inside the box [7, 9, 11, 12, 14, 15]. It appears to be most interesting to assume that not only the electron but also the nucleus moves inside it. The purpose of this paper is to discuss such a model in the simplest possible ways. In Sec. 2 we outline the model and write the Schrödinger equation in a dimensionless form. In Sec. 3 we obtain the ground-state energy approximately by means of first-order perturbation theory and compare it with the one for the clamped-nucleus case. In Sec. 4 we resort to a somewhat more elaborate variational function. Finally, in Sec. 5 we summarize and discuss the results.

2. The model

The Hamiltonian operator for a nonrelativistic hydrogen-like atom is

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ \hat{T} &= -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_n}\nabla_n^2 \\ V(r) &= -\frac{Ze^2}{4\pi\epsilon_0 r}\end{aligned}\tag{1}$$

where m_e and m_n are the masses of the electron and nucleus located at \mathbf{r}_e and \mathbf{r}_n with charges $-e$ and Ze , respectively, $r = |\mathbf{r}|$, $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_n$, ϵ_0 is the vacuum permittivity and ∇^2 denotes the Laplacian in the coordinates indicated by the subscript.

In the case of the free atom we separate the motion of the center of mass from the internal one by means of a well-known change of variables and obtain

$$\begin{aligned}\hat{H} &= \hat{H}_{CM} + \hat{H}_{int} \\ \hat{H}_{CM} &= -\frac{\hbar^2}{2M}\nabla_{CM}^2, \quad M = m_e + m_n \\ \hat{H}_{int} &= -\frac{\hbar^2}{2m}\nabla^2 + V(r), \quad m = \frac{m_e m_n}{M}\end{aligned}\tag{2}$$

where ∇^2 and ∇_{CM}^2 are the Laplacians for the variables \mathbf{r} and $\mathbf{r}_{CM} = (m_e \mathbf{r}_e + m_n \mathbf{r}_n)/M$, respectively, and m is the reduced mass. Thus, we can factor the energy states of the free hydrogen atom as $\psi(\mathbf{r}_e, \mathbf{r}_n) = \psi_{CM}(\mathbf{r}_{CM})\psi_{int}(\mathbf{r})$ and solve the Schrödinger equation

for \hat{H}_{int} in the usual way [24, 25]. The eigenfunctions and eigenvalues of \hat{H}_{int} provide all the physical properties of the isolated atom, such as, for example, the spectral lines, selection rules, etc. [24, 25].

If the atom is confined to a spherical box of radius R with impenetrable walls then the states should vanish when either $r_e = R$ or $r_n = R$ and, consequently, the above separation is not possible as discussed by Tanner [13] and Amore and Fernández [23] for the harmonic oscillator. The reason is that the variables \mathbf{r}_{CM} and \mathbf{r} are unsuitable for the boundary conditions that are naturally given in terms of \mathbf{r}_e and \mathbf{r}_n .

The positions of the electron and nucleus in the box are completely determined by six variables. We conveniently choose r_e , r_n and r (the sides of a triangle) plus three angles for the orientation of the triangle in space. The S states (those with zero angular momentum) depend only on the three radial variables: $\psi(r_e, r_n, r)$. In fact, if we take into account that

$$\begin{aligned}\nabla_e \psi &= \frac{\mathbf{r}_e}{r_e} \frac{\partial \psi}{\partial r_e} + \frac{\mathbf{r}}{r} \frac{\partial \psi}{\partial r} \\ \nabla_n \psi &= \frac{\mathbf{r}_n}{r_n} \frac{\partial \psi}{\partial r_n} - \frac{\mathbf{r}}{r} \frac{\partial \psi}{\partial r}\end{aligned}\tag{3}$$

then we realize that $\psi(r_e, r_n, r)$ has zero angular momentum:

$$(\mathbf{r}_e \times \nabla_e + \mathbf{r}_n \times \nabla_n) \psi = \frac{(\mathbf{r}_e - \mathbf{r}_n) \times \mathbf{r}}{r} \frac{\partial \psi}{\partial r} = 0\tag{4}$$

In order to simplify the calculation we first make the change of variables $\mathbf{r}'_e = \mathbf{r}_e/R$ and $\mathbf{r}'_n = \mathbf{r}_n/R$ that leads to the dimensionless Hamiltonian operator

$$\begin{aligned}\hat{H}_d &= \frac{m_e R^2}{\hbar^2} \hat{H} = -\frac{1}{2} \nabla_e'^2 - \frac{\beta}{2} \nabla_n'^2 - \frac{\lambda}{r'} \\ \beta &= \frac{m_e}{m_n}, \quad \lambda = \frac{m_e Z e^2 R}{4\pi\epsilon_0 \hbar^2}\end{aligned}\tag{5}$$

The states of this dimensionless system vanish when either $\mathbf{r}'_e = 1$ or $\mathbf{r}'_n = 1$. From now on we omit the primes on the dimensionless quantities but keep in mind that lengths, masses and energies are measured in units of R , m_e , and $\hbar^2/(m_e R^2)$, respectively. For example, $1/\beta$ is the nuclear mass in such units.

3. Perturbation theory

For simplicity we restrict ourselves to the ground state and a small box radius. If λ is a small parameter then we can try perturbation theory in terms of the unperturbed or reference Hamiltonian $\hat{H}_d^0 = \hat{H}_d(\lambda = 0)$. The perturbation is therefore given by the interaction between the particles $\hat{H}_d' = -1/r$. The unperturbed ground state is

$$\varphi(r_e, r_n) = 2 \frac{\sin(\pi r_e) \sin(\pi r_n)}{r_e r_n} \quad (6)$$

Therefore, the expectation value of \hat{H}_d with this function gives us the energy of the ground state corrected through first order of perturbation theory. Besides, according to the variation principle such approximate energy will be an upper bound to the exact one [24, 25].

The calculation is reminiscent of that for the helium atom under the clamped-nucleus approximation and we may therefore profit from well-known results. The calculation of the expectation value of the kinetic energy is straightforward, and there are various ways of calculating the expectation value of $1/r$ [24, 25]. Here, we resort to the expansion of $1/r$ in terms of Legendre polynomials that leads to the simple integral [24]

$$\begin{aligned} \int \frac{\varphi(r_e, r_n)^2}{r} d\tau_e d\tau_n &= 16\pi^2 \left[\int_0^1 \int_0^{r_e} \varphi(r_e, r_n)^2 r_e r_n^2 dr_n dr_e \right. \\ &\quad \left. + \int_0^1 \int_{r_e}^1 \varphi(r_e, r_n)^2 r_e^2 r_n dr_n dr_e \right] \end{aligned} \quad (7)$$

Since the analytical expression is rather cumbersome we just show the numerical result:

$$\begin{aligned} \epsilon(\lambda) &= \frac{\pi^2(\beta + 1)}{2} - 1.786073167\lambda \\ &= 4.934802200(\beta + 1) - 1.786073167\lambda \end{aligned} \quad (8)$$

Computer algebra systems are nowadays available in the science departments of most universities because they are invaluable teaching tools. This problem may be useful for motivating the students to resort to such software.

We can obtain simple analytical expressions by means of the even simpler trial function

$$\varphi(r_e, r_n) = 30(1 - r_e)(1 - r_n) \quad (9)$$

that leads to a quite similar result

$$\begin{aligned} \epsilon(\lambda) &= 5(\beta + 1) - \frac{25\lambda}{14} \\ &= 5(\beta + 1) - 1.785714285\lambda \end{aligned} \quad (10)$$

It is interesting to compare the results for this model with those for the hydrogen atom with the nucleus clamped at the center of the box. If we calculate the expectation value of the dimensionless Hamiltonian operator (notice that we use the same units as before)

$$\hat{H}_{dH} = -\frac{1}{2}\nabla^2 - \frac{\lambda}{r} \quad (11)$$

with the approximate trial function $\varphi(r) = \sqrt{30}(1 - r)$ we obtain

$$\epsilon_H(\lambda) = 5 - \frac{5\lambda}{2} \quad (12)$$

For comparison we also consider the unperturbed ground state

$$\varphi(r) = \sqrt{2} \frac{\sin(\pi r)}{r} \quad (13)$$

that leads to the first-order dimensionless energy

$$\begin{aligned} \epsilon_H(\lambda) &= \frac{\pi^2}{2} - 2.437653392\lambda \\ &= 4.934802200 - 2.437653392\lambda \end{aligned} \quad (14)$$

Obviously, these results are valid for sufficiently small values of λ . After contrasting equations (12) and (14) with more accurate results [21] we conclude that present first-order estimates are acceptable for $\lambda \lesssim 1$. In principle, we may assume that the accuracy of present moving-nucleus results are as accurate as the clamped-nucleus ones for $\lambda \lesssim 1$. If this is true, then our results suggest that the energy of the moving-nucleus model is larger than the clamped-nucleus one ($\epsilon(\lambda) > \epsilon_H(\lambda)$), at least for sufficiently small box radii. The difference does not come mainly from the kinetic energy of the nucleus that is

proportional to $\beta \approx 1/1836$ but from the electron–nucleus interaction. This conclusion is consistent with earlier variational results that show that the smallest energy takes place when the nucleus is clamped at the center of the sphere and increases as it approaches the wall [15]. Fig. 1 shows the approximate energies given by equations (8), (10), (12) and (14) for $\lambda \leq 5$ as well as accurate numerical energies for the clamped nucleus model calculated by a straightforward power-series method [21].

The critical value of λ defined by $\epsilon_H(\lambda_c) = 0$ estimated from the first-order perturbation energy (14) $\lambda_c \approx 2$ is about 9% larger than the actual value $\lambda_c = 1.835246330$ that one easily obtains by means of the method already mentioned above or from perturbation theory of greater order [21]. For the moving–nucleus model our approximate expressions (8) and (10) predict $\lambda_c \approx 2.8$ and we expect that its error is of comparable magnitude.

4. Variational method

We can improve the results of the preceding section by means of the variational method. To this end we propose the trial function

$$\varphi(r_e, r_n, r) = N(\alpha)(1 - r_e)(1 - r_n)e^{-\alpha r} \quad (15)$$

where α is a variational parameter and $N(\alpha)$ an appropriate normalization factor. Since it has the correct asymptotic behaviour $e^{-\alpha r}$ for the free atom, we expect it to yield accurate energies for large values of λ . More precisely, we expect that it yields the exact energy of the ground state of the free hydrogen

$$\lim_{\lambda \rightarrow \infty} \frac{\epsilon}{\lambda^2} = -\frac{1}{2(1 + \beta)} \approx -\frac{1}{2} \quad (16)$$

By means of a straightforward but tedious calculation we prove that

$$\begin{aligned} \hat{H}_d \varphi = & -\frac{1}{2} \left(\frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e} \frac{\partial}{\partial r_e} + \frac{r_e^2 - r_n^2 + r^2}{r_e r} \frac{\partial^2}{\partial r_e \partial r} \right) \varphi \\ & - \frac{\beta}{2} \left(\frac{\partial^2}{\partial r_n^2} + \frac{2}{r_n} \frac{\partial}{\partial r_n} + \frac{r_n^2 - r_e^2 + r^2}{r_n r} \frac{\partial^2}{\partial r_n \partial r} \right) \varphi \\ & - \frac{1 + \beta}{2} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \varphi - \frac{\lambda}{r} \varphi \end{aligned} \quad (17)$$

It follows from $r^2 = r_e^2 + r_n^2 - 2\mathbf{r}_e \cdot \mathbf{r}_n$ and $-r_e r_n \leq \mathbf{r}_e \cdot \mathbf{r}_n \leq r_e r_n$ that $|r_e - r_n| \leq r \leq r_e + r_n$. Therefore, we can calculate all the integrals that are necessary for the variational approach by means of the simple recipe [26]

$$\begin{aligned} \int \int \int f(r_e, r_n, r) d\tau = & \int_0^1 \int_0^{r_e} \int_{r_e-r_n}^{r_e+r_n} f(r_e, r_n, r) r_e r_n r dr_e dr_n dr \\ & + \int_0^1 \int_0^{r_n} \int_{r_n-r_e}^{r_e+r_n} f(r_e, r_n, r) r_e r_n r dr_n dr_e dr \end{aligned} \quad (18)$$

The calculation of the variational energy is simple but tedious and yields rather cumbersome results. In what follows we simply outline the main steps. First, notice that

$$\epsilon(\alpha, \lambda) = \langle \hat{H}_d \rangle = \langle \hat{T} \rangle(\alpha) - \lambda \langle 1/r \rangle(\alpha) \quad (19)$$

is a linear function of λ . Therefore, instead of calculating $\alpha(\lambda)$ from the minimum condition $\partial\epsilon(\alpha, \lambda)/\partial\alpha = 0$ we derive an analytical expression for $\lambda(\alpha)$ and a parametric expression for the variational energy: $\epsilon(\alpha, \lambda(\alpha))$. One can easily carry out this calculation by means of a computer algebra system.

Fig. 2 shows approximate values of ϵ/λ^2 obtained from the trial functions (9) and (15). We appreciate that there is a satisfactory agreement for $\lambda \lesssim 1$ as expected but it seems that our earlier prediction of the critical value λ_c was not as accurate as we believed. The variational function (15) yields the more accurate value $\lambda_c = 2.262$ that differs 21% from our earlier estimation. We also realize that the variational energy approaches the exact free-atom energy (16) as λ increases.

In passing, we mention that the variational calculation confirms the earlier perturbation result that the energy of the moving-nucleus atom is larger than the one with the nucleus clamped at origin.

5. Conclusions

Tanner [13] proposed a pedagogical discussion of the effect of the boundary conditions on the separability of the degrees of freedom of a confined system. However, he did not show any result for the one-dimensional harmonic oscillator that he chose as an

illustrative example. Later Amore and Fernández [23] discussed that model in more detail. In this article we extended those arguments to the hydrogen atom and carried out simple approximate calculations for the ground state by means of straightforward first-order perturbation theory and a more accurate variational approach. It has been our purpose to show how to do the calculation using well-known techniques already applied to the helium atom with the clamped-nucleus approximation. Our analysis shows that it is not possible to separate the Schrödinger equation in the usual way in terms of internal and center-of-mass coordinates \mathbf{r} and \mathbf{r}_{CM} , respectively, because the boundary conditions are given in terms of the electron and nucleus coordinates \mathbf{r}_e , and \mathbf{r}_n , respectively. Our approximate results show that the energy is greater when the nucleus moves than when it is clamped at the center of the spherical box and that the difference does not come mainly from the kinetic energy of the moving nucleus that is considerably smaller than the electronic one. Present results based on perturbation theory are limited to a small box radius or strong confinement but the variational ones are valid for all box sizes and yield the free-atom energy when $R \rightarrow \infty$. Although it is relatively easy to carry out perturbation calculations of large order for the clamped-nucleus model [21], the treatment of the moving-nucleus case is considerably more complicated. The variational method appears to be a better choice. It can be improved as in the case of the Helium atom by means of a Hylleraas-like expansion [26] for the trial function $\varphi(r_e, r_n, r)$.

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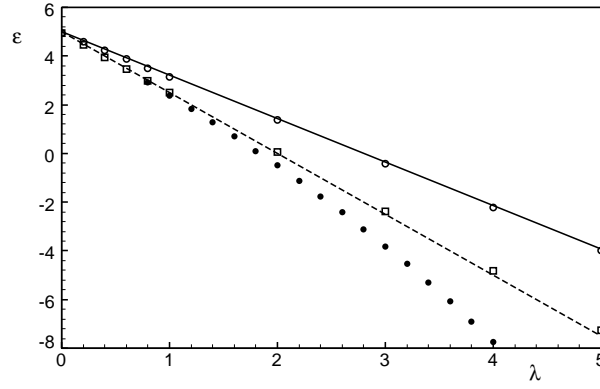


Figure 1. Results from equations (8) (circles), (10) (solid line), (12) (dashed line), (14) (squares) and power series (filled circles).

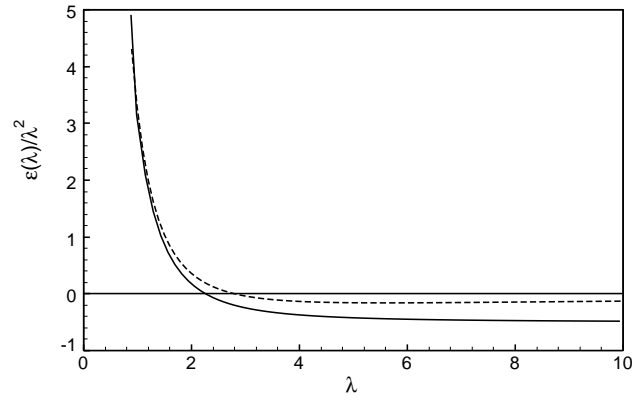


Figure 2. Approximate values of $\frac{\epsilon(\lambda)}{\lambda^2}$ obtained from the trial functions (9) (dashed line) and (15) (solid line).